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PREPARATION OF THE FLUOROSULFONATES:

$KI(SO_3F)_4$ ,  $KBr(SO_3F)_4$ ,  $SnCl(SO_3F)_3$ , and  $CrO_2(SO_3F)_2$

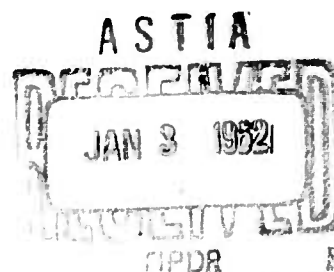
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1961

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Preparation of the Fluorosulfonates:  $\text{KI}(\text{SO}_3\text{F})_4$ ,  $\text{KBr}(\text{SO}_3\text{F})_4$ ,

$\text{SnCl}(\text{SO}_3\text{F})_3$  and  $\text{CrO}_2(\text{SO}_3\text{F})_2$

By Max Lustig and George H. Cady

It is known that peroxydisulfuryl difluoride,  $\text{S}_2\text{O}_6\text{F}_2$ , reacts with some chlorides to replace chlorine by the fluorosulfonate group<sup>1</sup>.

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1. Jean'ne M. Shreeve and George H. Cady, J. Am. Chem. Soc. 83, 3000, 1961.  
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This type of reaction has now been used to prepare  $\text{SnCl}(\text{SO}_3\text{F})_3$  from  $\text{SnCl}_4$  and  $\text{CrO}_2(\text{SO}_3\text{F})_2$  from  $\text{CrO}_2\text{Cl}_2$ . It has also been shown that  $\text{S}_2\text{O}_6\text{F}_2$  fails to replace the halogen in  $\text{KBr}$  or  $\text{KI}$  when reacting at about room temperature. Instead of this the complex salts,  $\text{KBr}(\text{SO}_3\text{F})_4$  and  $\text{KI}(\text{SO}_3\text{F})_4$ , are formed.

#### Experimental

Materials. - Peroxydisulfuryl difluoride was prepared by the method of Dudley et al by passing a stream of  $\text{SO}_3$  containing a slight excess of  $\text{F}_2$  through a "catalytic" reactor<sup>2,1</sup> at  $165^\circ$  using dry  $\text{N}_2$

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2. K.B. Kellogg and George H. Cady, J. Am. Chem. Soc., 70, 3086 (1948).  
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as a carrier. The product was purified by pumping away fluorine fluoro-sulfonate and other volatile impurities while the material was held at  $-78^\circ$ .<sup>1</sup> The potassium halogenides were of analytical quality.

Stannic chloride and cromyl chloride were purified by vacuum distillation using the same vacuum line employed for the synthesis of the various fluorosulfonates.

Potassium Tetrakis(fluorosulfonato)iodate(III). - An excess of peroxydisulfuryl difluoride was distilled into a weighed and cold bulb containing 0.271 mmoles of KI. The bulb was then allowed to warm. A mildly exothermic reaction began to occur just below room temperature. At first the solid became brown in color. After several hours, however, it became white. The excess reagent was distilled out of the bulb, and the weight of the product was that of 0.267 mmoles of  $KI(SO_3F)_4$ .

When a solution of sodium hydroxide was added, the product reacted according to the equation



rapidly and exothermically. Further hydrolysis of the fluorosulfonate to sulfate and fluoride ions took place by prolonged heating. The iodate was determined by iodometry using the "dead stop" potentiometric method.<sup>3</sup> The sulfate was determined as barium sulfate and the fluoride

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3. G. Wernimont and F.F. Hopkinson, Ind. Eng. Chem., Anal. Ed., 12, 308 (1940).  
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as triphenyltin fluoride.<sup>4</sup> Found: iodate, 0.184 mmoles; sulfate,

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4. Nelson Allen and N. Howell Furman, J. Am. Chem. Soc., 54, 4625 (1932).  
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1.13 mmoles; fluoride, 1.09 mmoles. Calcd: iodate, 0.182 mmoles; sulfate and fluoride, 1.08 mmoles.

Potassium tetrakis(fluorosulfonato)iodate(III) is a white solid which melts at 167-8° with slight decomposition yielding a green material which may be  $ISO_3F^5$ . This salt does not react with  $F_2$  at 100°.

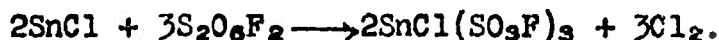
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5. John E. Roberts and George H. Cady, J. Am. Chem. Soc. 82, 352 (1960).  
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Potassium Tetrakis(fluorosulfonato)bromate(III). - This salt was prepared in the same way as potassium tetrakis(fluorosulfonato)iodate(III) except that the reaction flask was closed by a break-seal rather than a stopcock. As the reactants warmed a chemical change started at about  $0^{\circ}$ . At first the solid became orange in color; then it slowly turned white. The flask was heated to  $50^{\circ}$  for several days to insure complete reaction. 4.697 mmoles of KBr yielded a solid residue having the weight of 4.628 mmoles of  $\text{KBr}(\text{SO}_3\text{F})_4$ .

The salt reacted with sodium hydroxide solution yielding oxygen and some bromine, the latter being quickly absorbed by the solution. The salt also produced some oxygen when it reacted with a solution containing a large excess of potassium iodide. In both cases the quantity of oxygen produced varied from one run to another. The solution from the alkaline hydrolysis was made acidic and then treated with  $\text{NaHSO}_3$  to reduce  $\text{BrO}_3^-$  to  $\text{Br}^-$ . The sulfur dioxide was then removed by prolonged boiling. Bromide ion was determined as  $\text{AgBr}$ ; sulfate as  $\text{BaSO}_4$  and fluoride as triphenyltin fluoride. Found: 15.4% Br, 24.7% S, 14.3% F. Theoretical: 15.51% Br, 24.89% S, 14.75% F.

Potassium tetrakis(fluorosulfonato)bromate(III) is a white solid which begins to decompose at  $100^{\circ}$  giving a dark red liquid having the appearance of  $\text{BrSO}_3\text{F}$ .<sup>5</sup>

Chlorotris(fluorosulfonato)tin. - This compound was prepared by contacting tin(IV) chloride with a large excess of peroxydisulfuryl difluoride in a sealed tube equipped with a break-seal attachment. A mild reaction took place just below room temperature and was complete within a few minutes. The reaction proceeded as follows:



It was found that heating the reactants at  $100^{\circ}$  for several days

achieved no further replacement of the chlorine. 0.518 mmoles of  $\text{SnCl}_4$  yielded a weight of the above compound corresponding to 0.517 mmoles.

The volatile material remaining after the reaction was distilled and was shown by vapor density and infrared spectra to contain  $\text{Cl}_2$ ,  $\text{S}_2\text{O}_6\text{F}_2$  and a trace of an unidentified substance. After hydrolysis of the solid material in sodium hydroxide solution, chloride and sulfate were determined gravimetrically as  $\text{AgCl}$  and  $\text{BaSO}_4$ , respectively. Found: 7.84% Cl, 21.0% S. Theoretical: 7.87% Cl, 21.3% S.

Chlorotri(fluorosulfonato)tin is a white solid decomposing at about  $167^\circ$ .

Dioxobi(fluorosulfonato)chromium(VI). - Chromyl chloride was found to react with excess  $\text{S}_2\text{O}_6\text{F}_2$  at room temperature as follows:



0.362 mmoles of  $\text{CrO}_2\text{Cl}_2$  yielded a solid having the weight of 0.345 mmoles of  $\text{CrO}_2(\text{SO}_3\text{F})_2$ . Found: 14.23% Cr, 17.8% S, 0.99% Cl. Theoretical: 14.74% Cr, 18.17% S, 0.00% Cl. Chromium was determined by iodometric analysis involving the chromate ion formed by alkaline hydrolysis of the solid. Chloride and sulfate were determined as  $\text{AgCl}$  and  $\text{BaSO}_4$ , respectively.

Dioxobis(fluorosulfonato) chromium(VI) is a dark brown, slightly volatile solid which decomposes very slowly at room temperature into a greenish compound. Hydrolysis of an aged sample yielded a yellow solution and a small amount of green flocculent precipitate resembling chromium(III) hydroxide.

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